Synthesis and Applications of Polyacrylate based Water White Clear Polymeric Material Fortified with Carbon Nanotubes for Durable, Protective and Corrosion Resistance Coatings Used in Applied Automobile Industry

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Summary: Acrylates are esters of acrylic acid formed by the reaction of acrylic acid with alcohols. These acrylic esters were produced by polymerization of combination with different acrylic monomers to produce the materials with enhanced characteristics for coating applications. The acrylate-based polymers were prepared by varying the nature and ratios of the monomers. Moreover, the properties of the polymeric materials were further improved by compositing with the nano-fillers i.e. carbon nanotubes. Further, the materials were coated on different surfaces to evaluate the coating characteristics by standard analytical procedures. Composition and morphology of the materials were characterized by different spectroscopic techniques. Polyacrylate based polymers were synthesized by step growth polymerization using different types of monomers moieties (5 different types of acrylic monomer along with one functional monomer and an aromatic monomers) to enhance coating properties and to enhance dispersion of carbon nanotubes. Characterization was done by FTIR (Fourier Transform Infra-Red) and UV-Vis spectroscopy. Study of polymeric coating was done on different surfaces by different techniques like Barcol Hardness, Gloss Test, Salt Spray Test, Cross Hatch Test and Mandrel Dent Measurement as given in standard ASTM methods. The results revealed better adhesion, crack resistance, and abrasion resistance. The graphical abstract is given below as Fig-1.

Graphical Abstract:
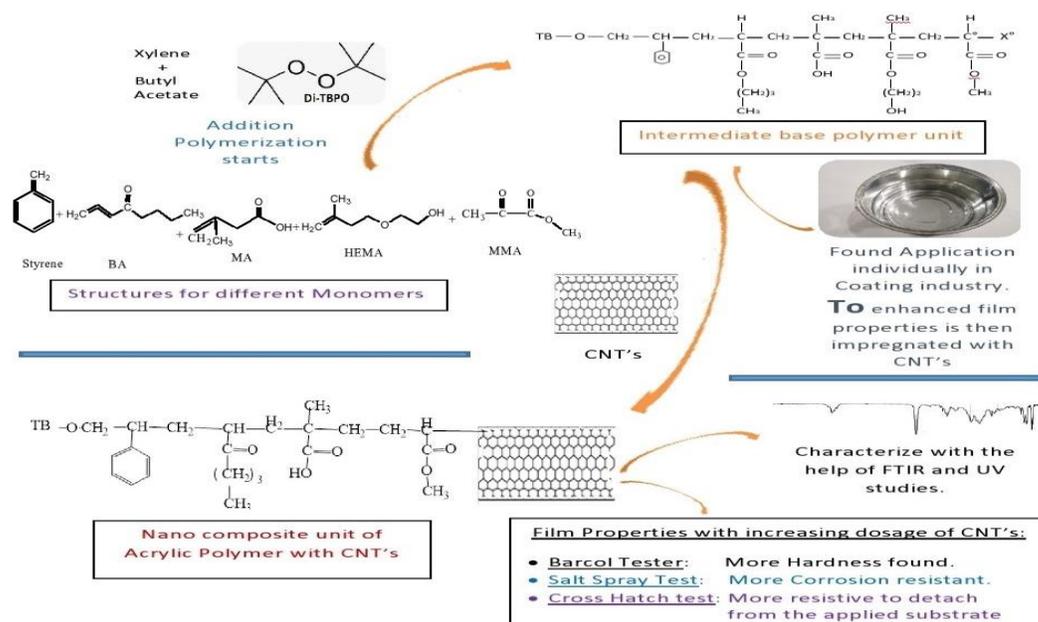
Fig. 1:   Graphical Abstract

Key words: Acrylates, Nano-fillers, Polymeric coatings, Corrosion resistance, Penetration of coating material, Carbon nanotubes dispersion in polymeric solution, Scratch resistance.

Introduction:

The term coating and paint seems synonymous but coating refer to as application like automobiles, beverages bottles and furniture and paint refer to architectural coating such as house paint, wall and ceiling as artist paint [1]. Functional coatings are often used to protect the surfaces. The surfaces like wood, plastic or metal are protected from environmental degradation. The devastations of nature are due to a hostile environment. Such environment can cause variety of damages. Wear and tear occurs through rusting, erosion, and etc. Such coating could also protect the expensive parts. Which are the parts of an assembly that are difficult to reach for maintenance [2]. Fillers are used to enhance the coating properties along with polymer matrix [3]. Protective films along with nano-composites are widely developed on different metals which help to reduce corrosion [4]. Now a day much attention is being paid on polymeric materials for the development of environment friendly coating for protection. Smart good looking coating that is typically stripper than a piece of office paper [5]. Particularly in superficial coverings, polyacrylate formulations are toughened by copolymerizing the acrylate with other monomers. Such as methyl methacrylate or styrene and silica nano-system are used for copolymerization [6]. Similarly, some polyurea based coatings have been developed to improve thermal conductivity and resistance to corrosion by using nano silver compounds [7]. Rheologies gave facts for level of distribution and web arrangement of filler units [8]. The sticking performance of material, uncross binded butyl acrylate-methyl acrylate copolymer on diverse surfaces. For example stainless steel, polyethylene, glass and Si-wafer have been examined. It could be done by consuming a series of analysis tests and real-time video-optical snapping. Tack and stress peak standards rise. The final number of cavities and cavity growth rate decreases as well. It happens with increasing surface energy of the substrate due to better wetting [9]. In literature, it is well predicted by the terminal copolymerization model using the kinetic parameters computationally determined [10]. Acrylic esters have two functional groups. Those are responsible for reactions to occur. Mainly the ester group and double bond do this function. Reactions on the ester group are also carried out. But such under conditions which avoid polymerization of the double bond [11]. Anticorrosion and superhydrophobic double layered coatings can be developed by using amine and aldehyde based benzoxazine to protect metals like steel [12]. In general, the rate of polymerization must be controlled. This in turn controls the average molar mass. It could be achieved by controlling the initiator and monomer concentration. Moreover, reaction temperature is also necessary to optimized [13]. Methyl, ethyl and n-butyl acrylates and methacrylates are found to form high molecular mass compounds. They make them quite easily by emulsion polymerization [14]. The use of co-emulsifier (long chain alkanes, ammonium salts or block copolymer of ethylene and propylene oxide) can produce micro-emulsion. They are thermodynamically stable systems. Because, their average particle size of is about 100 mm [15]. Alkyd resin along with carbon nanotubes used for developing anticorrosion coating [16]. Acrylate block copolymer (MMA-b-MMA) was used as surfactant in emulsion polymerization of acrylate monomers [17]. The materials were polymerized by various alkyl acrylates, methyl acrylates, ethyl acrylates, butyl /acrylates, hexyl acrylates and 2-ethylhexyl acrylate and alkyl methacrylates in micro emulsion [18]. Free radical polymerization HEMA were carried out using azobisisoboutyronitrile as initiator at the temperature range 60-70 ^{O}C. HEMA is water repellant, apparent dynamic and great clarity double functionality monomer. It is generally utilized as bonding agent and in polymeric forms in ample uses. The modification of polymer was carried out by 9-anthracenecarboxylic acid (9-ACA) via the esterification reaction between -OH of HEMA and -COOH of 9-ACA [19]. The widespread variety of acrylic monomers is presented which can be copolymerized to provide modify copolymers showing a wide features. Hydroxy ethyl meth acrylate, acrylic acid, methacrylic acid and glycidyl methacrylate are in form of various general illustrations [20]. To improve a appropriate covering films polymerization can be done via bulk, solution, suspension and emulsion polymerization techniques. The emulsion polymerization method has numerous discrete benefits. The physical state of emulsion system marks it simple to regulate the route. Thermal and viscosity difficulties are of minimum importance than in bulk polymerization. The greatest significance of this polymerization is that both high molecular weight and high reaction rate can be achieved concurrently. The production of emulsion polymerization can be engaged directly for coating, finishes, polishes and paints [21]. Carbon nanotubes are of pronounced attention because of their exceptional unification beneficial properties. Such features are high aspect ratio, ballistic electron transport, high current carrying capacity and high mechanical strength and stiffness. Bearing in mind these features, macroscopic carbon nanotubes (CNT) fibers are auspicious to substitute metallic electrical wires. They are ready to produce the leading really

artificial electrical conductors. That can be deployed on a large scale. The continual web construction shaped by networked MWCNTs and infiltrated fine clay stacks [22]. However wide spread use of carbon nanotubes is still challenging due to the processing difficulties, which have hindered the ability to take full advantage of their properties at the macroscopic scale [23]. A virtuous MWNT dispersal and great applications supplement in the development of a powerfully networking MWNT structure as specified by steady shear-viscosities standards [24]. A nanotube with small diameter mater may be less stable than a nanotube with a larger diameter [25]. Composite materials fabricated by carbon nanotubes are widely used to protect some alloys like magnesium alloys coatings significantly enhance mechanical properties have been recently reported [26].

Experimental

Method

According to the given Scheme # 01, the ratios of hydroxy ethyl methacrylate and methyl methacrylate were used as per selection reported in Table-1 and mechanism of reaction as in Fig. 2.

The monomers were loaded as per above given ratio in Pyrex glass vessel of 2.0 liters capacity fitted with condenser, thermometer, and having a heating source. The required temperature was 80-82 ^{O}C to add the initiator by using the dropping funnel of 200 mL capacity. So, it was taken 3-3.5 hrs to complete the addition of initiators in five equal intervals. After which, a digestion time of 1 hour was allowed to complete the reaction of whole monomers. Then, the addition of CNT in the polymer matrix was carried out per given ratios mentioned in column of filler percentage. The material was cooled down to 45-50 ^{O}C and labeled the product as S1-S5.

Dispersion of Carbon nanotubes in polymer

Carbon nanotubes are classic objects in nanotechnology, bundle like structures with very complicated morphologies which causes very poor solubility in water and solvents. Carbon nanotubes were dispersed in polymeric material by using 1% of CNTs which was followed by ultrasonic homogenization by using ultrasonic homogenizer for approximate 3-5 minutes

Table-1: Chemical composition

Sr#	Xylene (gm)	Styrene (gm)	Methyl Meth Acrylate (gm)	Butyl Acrylate (gm)	Hydroxy Ethyl Meth Acrylate (gm)	Meth acrylic acid (gm)	Butyl Acetate (gm)	Total (gm)	Carbon nano tubes %age
S-1	314	10	256	124	12	3	105	568	0.1
S-2	314	10	256	124	12	3	105	579	0.2
S-3	314	10	256	124	12	3	105	592	0.3
S-4	314	10	256	124	12	3	105	601	0.4
S-5	314	10	256	124	12	3	105	616	0.5

Table-1: Details of FTIR Spectral data

S-1	S-2	S-3	S-4	S-5	CNTs	Description-I	Description-II
691.49	692.46	688.6	692.46	691.49	634.58	C-H out of plane often near 690 RCH=CHR	
699.21	699.21	692.46	700.17	700.17	646.15	C-H out of plane	
743.57	744.54	694.39	744.54	744.54	779.24	C-H	meta disubstituted-Aromatic
768.65	759.97	698.24	759	758.04	900.76	C-H	meta disubstituted-Aromatic
796.61	769.61	700.17	769.61	768.65	937.4	C-H	meta disubstituted-Aromatic
1163.1	797.58	707.89	796.61	1145.74	979.84	C-H	meta disubstituted-Aromatic
1192.03	985.64	745.5	1030.97	1161.17	1224.8	Alkenes(RCH=CH2)	
1242.18	1030.01	754.18	1065.69	1164.06	1305.81	Alkyl Ether(R-O)	
1453.39	1120.66	759.97	1120.66	1191.06	1323.17	Diaryl Ethers(Ar-O-Ar)	
1465.93	1163.1	769.61	1146.7	1193.96	1336.67	Diaryl Ethers(Ar-O-Ar)	
1495.82	1192.03	796.61	1162.13		1371.39	DiarylEthers(Ar-O-Ar)	
1728.25	1242.18	1121.63	1192.03	Peak	1384.89	Alkyl Aryl Ethers	
	1272.08	1134.16	1215.17	691.49	1444.68	Alkyl Aryl Ethers	
	1300.04	1163.1	1240.25	700.17	1487.12	Cyclic Anhydrides	
	1436.03	1193.96	1267.25	744.54	1504.48	Alkyl	
	1453.39		1453.39	758.04	1566.2	Alkyl	
	1465.93		1464	768.65	1585.49	Alkyl	
	1726.32			1145.74	1645.28	Aromatic	
					1693.5		

Reaction mechanism

Styrene   BA   MA   HEMA   MMA

Xylene:

70-72 °C   **Butyl Acetate:** $H_3C - C - O - (CH_2)_3 - CH_3$

Di-TBPO: $H_3C - C - O - O - C - CH_3$
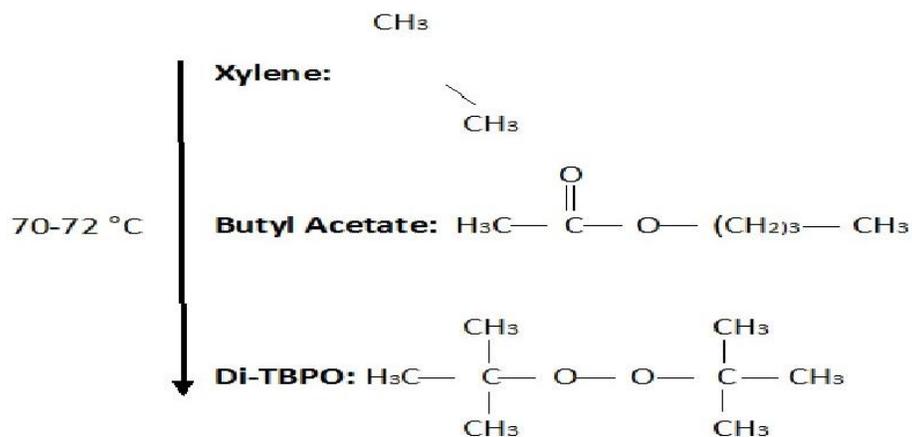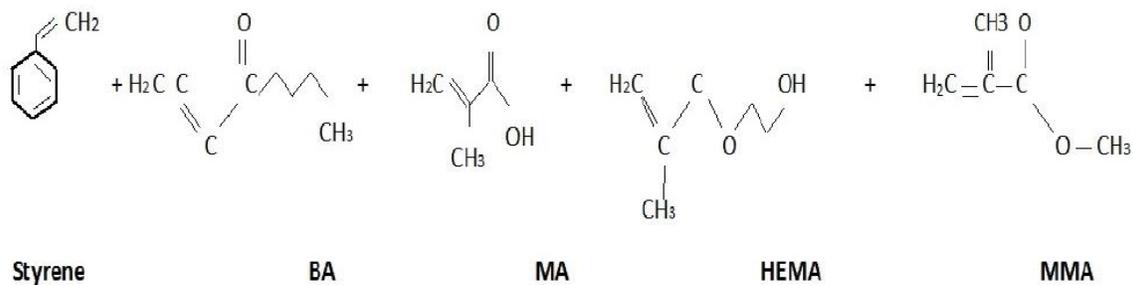
INITIATION STEP

At 70-72 °C

Di-TBPO: $CH_3 - C - O - O - C - CH_3$

**PROPAGATION STEP**

BA

Fig. 1:   Reaction Mechanism
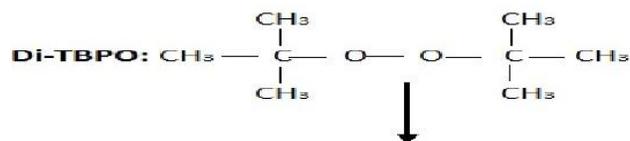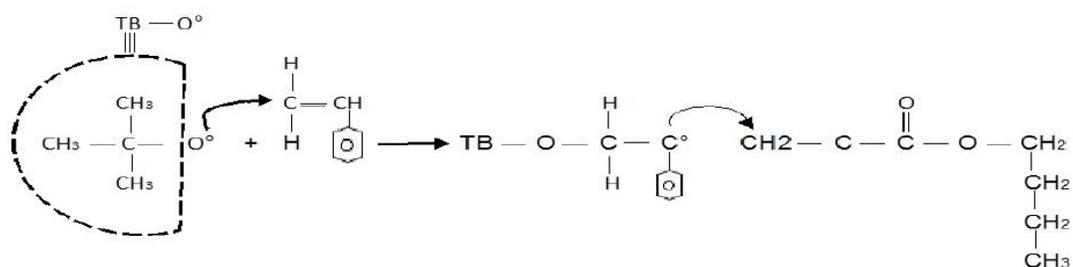
Results and Discussion
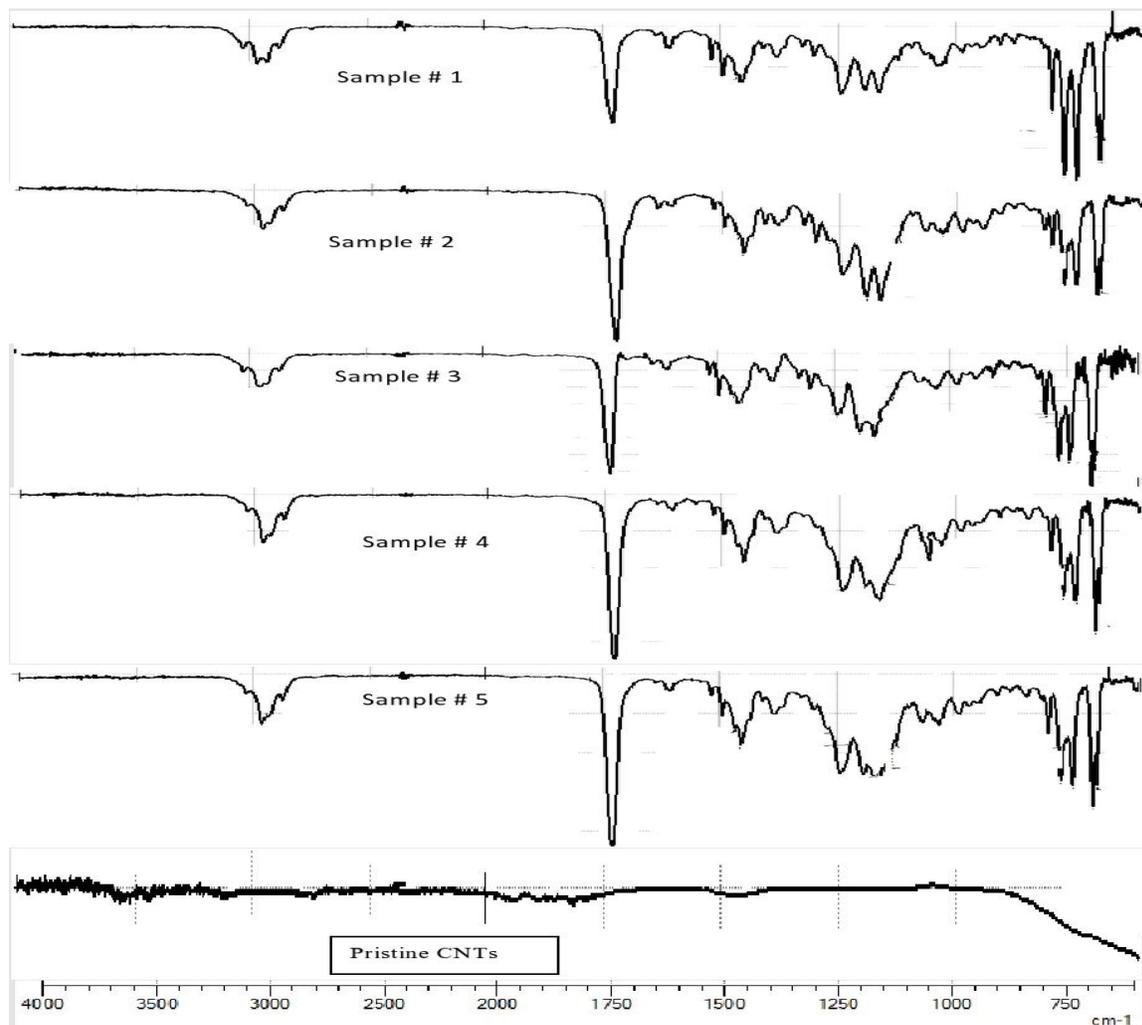
Fig. 2:   FTIR Spectra

FTIR Spectra of samples:

All the reagents including methyl methacrylate (MMA) and hydroxy ethyl methacrylate (HEMA) was used in this scheme having variable quantity of carbon nanotubes. CNTs were used for the synthesis of polymeric coating material. The FTIR Studies convinced that the functional groups were repeated in these samples which were like unreacted peroxides and hydro-per oxides. The peaks were quite close to each other. The Peaks formed at wavenumber 2920-3000 cm^{-1} were due to C-H stretching vibrations showed the presence of unreacted peroxides and hydro-peroxides in the reaction mixture. It was also confirmed by having peaks at 1435-1470 cm^{-1} which may be due to C-H deformation vibrations of these peroxides and also due to C-H rocking vibrations at 1185-1200 cm^{-1}. The peak at 2920-3000 cm^{-1} was also

due to presence of aromatic unsaturated moiety present in the polymer. The C=O stretching vibration were shown at 1715-1750 cm^{-1} due to the presence of aliphatic carboxylic acid and aliphatic esters moieties present in the polymers. For the confirmation of ester presence, it was also found peaks at 1435-1470 cm^{-1} which was due to –CH$_2$. It was the deformation vibrations of this particular functional group. For methylene group present, it was found C-H scissoring vibrations at 1440-1480 cm^{-1}. The observation was the increasing amplitude of peak at 1030-1100 cm^{-1} due to the binding of CNTs with the base polymers (Modified CNTs). These region peaks were usually assigned to C-O-C stretching vibrations. Multiple peaks were observed at 995-1040 cm^{-1} and 700-900 cm^{-1} which were due to presence of aromatic C-H and -CH$_3$ group respectively in the polymer structures

Table-3: UV-Absorbance data

Sr No	Sample # 1 (nm)	Abs	Sample # 2 (nm)	Abs	Sample # 3 (nm)	Abs	Sample # 4 (nm)	Abs	Sample # 5 (nm)	Abs
1	536	0.142	844	0.082	775	0.052	780.5	0.114	781.5	0.079
2	783.5	0.143	803.5	0.083	833.5	0.053	841.5	0.115	841.5	0.08
3	558.5	0.143	794	0.083	727.5	0.053	825.5	0.115	813.5	0.08
4	841.5	0.144	685.5	0.084	591.5					
5	492.5	0.144	727	0.085	803					
6	692	0.144	741	0.086	673					
7	744.5	0.146	716	0.086	605					
8	890.5	0.156	890	0.093	743.5					
9	282.5	2.947	876	0.099	507.5					
10	289.5	3.07	266	2.839	250					
11	293.5	3.495	300	3.366	310					

Table-4: Barcol Hardness

Sample	Barcol Hardness
S-1	42
S-2	43
S-3	44
S-4	45
S-5	48

Fig. 4:   UV Spectra.
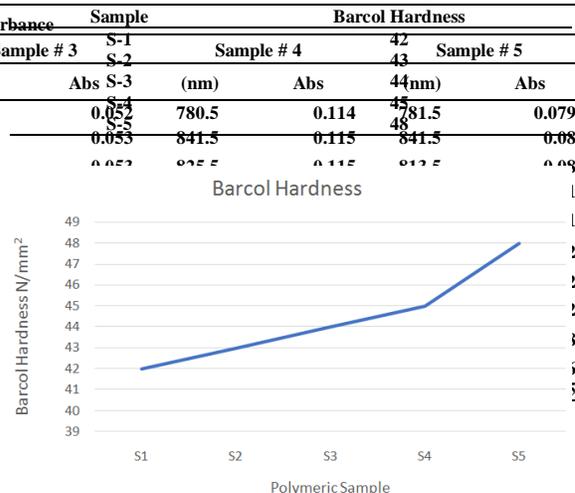
Fig. 3:   Barcol Hardness Testing

UV Absorbance Data

From the data of U.V. spectrum, it can conclude that pristine CNTs showed lambda max (λ_{Max}) at much higher wavelength which is 665 nm compared to the base polymer. In scheme 1, different samples were prepared with variable amount of CNTs for sample 1 containing the lowest while sample 5 has highest amount. So, it could be interpreted from this data that due to presence of CNTs, grafting was occurred with the base polymer as shown in the reaction mechanism resulted in the red shift as shown in Table-3 and Fig 4.

Barcol Hardness Test

Sample (1/16th of inch) was placed under Barcol tester and a uniform pressure was applied to the sample until the indication (dial) reached to the maximum depth of penetration. The depth of penetration was then converted into Barcol number mentioned in Table-4 and Fig 5 given below.

The Barcol hardness was performed by following ASTM D 2583, measured on a scale from 0 to 100 with the typical range between 50B and 90B. A measurement of 60B was roughly equivalent to the Shore hardness of 80D or Rockwell hardness M100.

Gloss Test

Gloss test was performed by BRDF-Bidirectional Reflectance Distribution Function. Individual gloss on Steel panels and wooden panels was given below in Table-5 and Fig 6.

Table-2: Gloss Test

Composition	Steel %age Gloss*	#Wood %age Gloss
S-1	105	7
S-2	105	7
S-3	104	7
S-4	104	6
S-5	98	5

*Self-Gloss 45%   #Self-Gloss 3%

Fig. 4:   Gloss Test.

Steel gave more gloss than wood; however addition of carbon nanotubes affected the gloss of final product.

Salt Spray Test

Salt spray test provided a controlled corrosive environment and helped in providing corrosion resistance information for the specimens of metals and stainless steel. Corrosion resistance of stainless steel was used for many uses in industrial, automotive and domestic applications. The data received for all developed materials was given in Table -6 and Fig 7.

Table-3: Salt Spray Test.

Composition	Corrosion Progress Hrs	Exposure Time-Un Coated -Hr	Exposure Time-Coated-Hrs
S-1	88	46	105
S-2	96	50	105
S-3	104	55	104
S-4	112	60	104
S-5	120	65	98
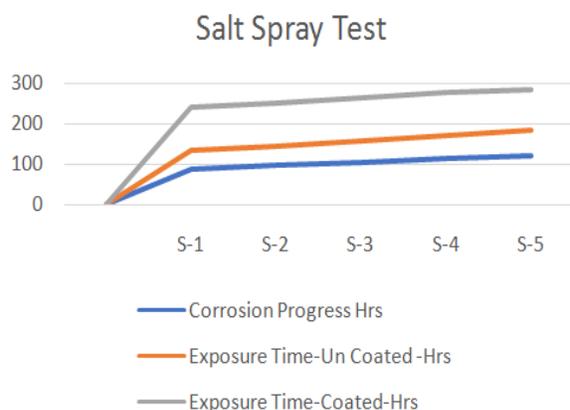
Fig. 5: Salt Spray Test

The values shown in the Table-10, elaborated the fact that coated films materials were able to bear more time than uncoated materials. It is also observed that CNTs added films endured more exposure time

Cross hatch test

This method helped in determining the coating resistance by separation from its applied substrate when incisions were made as far as the substrate shown in Table-7 and Fig. 8.

Cross hatch tests of different polymeric composition layers showed that polymeric compositions fall in range of 5B and 4B. From above it was obvious that CNTs S1 & S2 were giving much better results than other compositions.
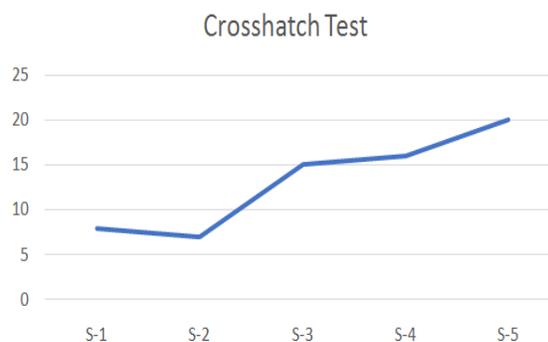
Fig. 6:   Cross hatch test.

Table-4: Cross hatch test

Composition	Crosshatch Test*
S-1	8
S-2	7
S-3	15
S-4	16
S-5	20

Manderal Bend Testing

The relationship between coating elongation at the interface with the base as a function of Manderal diameter was shown in below graph. This graph was a representative of a coating with thin sheen coating applicator 100 micron. The coated substrate was (coated side up) bent around Manderal and cracking was noted after applying a uniform force. The distance from the small end of the mandrel to the crack was determined visually and can be used graphically to determine the percent elongation. The angel of bending was 180º. Usually six Manderals having diameters ranging 25mm to 3.2mm were used. The panel was bent over the largest diameter Manderal and then immediately observed for cracking. If none occurs then next smaller mandrel was used and so on until failure was occurred. Coating failure was appeared by visual inspection and results were given in Table-8 and Fig 9.
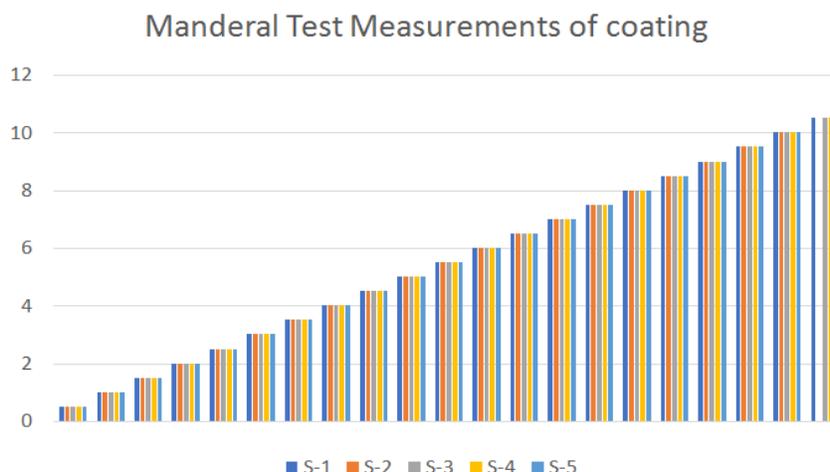
Fig. 7:   Manderal Bend Testing.

Table 5: Manderal Bend Testing.

							Manderal Test Measurements of coating														Result
S-1	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	Pass
S-2	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10		Pass
S-3	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	Hard
S-4	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	Hard
S-5	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	Hard

All above mentioned different polymeric compositions showed different bend tests results. Best one was that in which there was a combination of functional groups and a moderate ratio of carbon nanotubes, as given in S1 and S2 composition.

Conclusion

The acrylate copolymers were synthesized by varying the amounts and of ratios of methyl methacrylate, hydroxy ethyl methacrylate and carbon nanotubes. The properties like hardness, gloss, salt spray, tape test and flexibility were tested. Results revealed that film properties were varied by varying the ratios of monomers which affected other inherent and require properties of the polymer. For the specific coating application, the film was not so hard or soft with a gloss and better adhesion properties. From above results, it was evident that ratios of monomers imparted characteristic effect on the polymer film which further enhanced after the incorporation of carbon nanotubes. The S1 and S2 showed stable film formation. Whereas, other parameters were of more promising in nature for S2 compared with other polymeric combinations.

Author's Contributions

Sajjad Hassan performed the experimental work and Mirza Nadeem Ahmad supervised him and

Declaration of Competing Interest:

None

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